

PATENT SPECIFICATION

NO DRAWINGS

Inventor: HAROLD WEBSTER

897.698



Date of filing Complete Specification Sept. 9, 1959.

Application Date June 12, 1958.

No. 18789/58.

Complete Specification Published May 30, 1962.

Index at acceptance:—Class 2(3), C3X.

International Classification:—C07f.

COMPLETE SPECIFICATION

Improvements in the manufacture of Dialkyl Alkylphosphonothionates

We, NATIONAL RESEARCH DEVELOPMENT CORPORATION, a British Corporation established by Statute, of 1, Tilney Street, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the manufacture of the dialkyl alkylphosphonothionates, a number of which are used as insecticides.

The invention provides an improved process by which the dialkyl alkylphosphonothionates may be manufactured from the appropriate alkylphosphonous dichloride, the appropriate alcohol and sulphur.

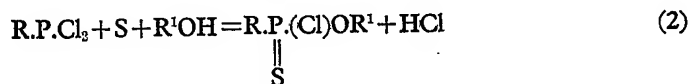
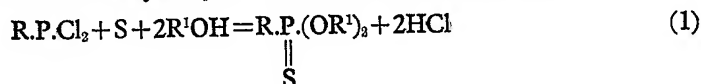
Hitherto the complete reaction has been carried out in more than one stage and it has been necessary to provide in the reaction vessel some additional substance with the reagents for removing the hydrogen chloride produced by the reaction from the reaction zone in order that the reaction may proceed to give satisfactory yields of the dialkyl alkyl-

phosphonothionate. Such processes have employed a solvent in which the reaction takes place and which has high sulphur and low hydrogen chloride solubility or alternatively have employed a hydrogen chloride acceptor such as a tertiary base.

The present invention provides a simple and rapid process by which the dialkyl alkylphosphonothionates may be synthesised in a single reaction vessel without the use or presence of any other substance to remove the hydrogen chloride produced.

It has been discovered that if a reaction mixture is formed of an alkylphosphonous dichloride, elemental sulphur and an alcohol and this mixture is maintained at a temperature in the region of its boiling point in the liquid state the hydrogen chloride produced as the reaction proceeds readily vaporises so that its concentration in the liquid reaction phase remains low and the reaction can proceed until a satisfactory yield of the dialkyl alkylphosphonothionate is obtained.

It has been established that the following three reactions take place:—



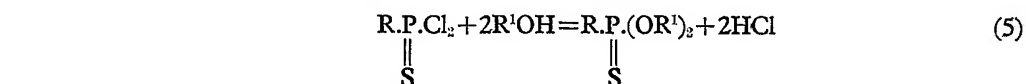
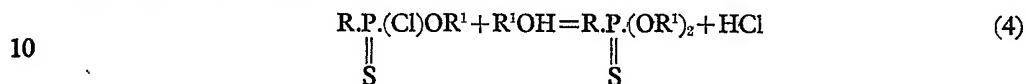
where R and R¹ represent C₁—C₄ alkyl groups.

In the earlier part of the reaction period all three reactions (1), (2) and (3) proceed, at first the reactions (2) and (3) predominate, the hydrogen chloride produced catalysing

the production of alkylphosphonothionic dichloride in accordance with reaction (3). The maintenance of the mixture at the elevated temperature close to its boiling point for a further period brings about an increase in the concentration of the dialkyl alkylphosphono-

thionate and a decrease in the concentration of alkyl alkylphosphonochloridothionate produced in accordance with reaction (2) and alkylphosphonothionic dichloride produced in accordance with reaction (3) as these two

intermediate products react with the alkanol to produce dialkyl alkylphosphonothionate respectively in accordance with the following reactions:—



As indicated by reaction equation (1), two mols of alkanol are required by the reaction for each mol of alkylphosphonous dichloride. The alkanol should not be present in excess of its stoichiometric proportion, and should preferably be present in less than its stoichiometric proportion, during the initial part of the reaction, to ensure that there is not an unnecessary amount of unreacted alkanol then present as this alkanol is a solvent for the hydrogen chloride produced. It is however also preferable for the alkanol to be present in at least stoichiometric proportions when the reaction is nearing completion.

When the process is carried out batchwise it is consequently advantageous for the alcohol to be added, preferably slowly, to a mixture of the alkylphosphonous dichloride and elemental sulphur at a temperature near to the boiling point of the mixture until the alcohol is present in at least stoichiometric proportions.

When the process is carried out in a continuous manner, it is important that the alcohol is not present for any significant time in stoichiometric excess and where the liquid alcohol and alkylphosphonous dichloride are supplied to sulphur in a reaction zone the rate of supply of these two reactants should be maintained with reasonable accuracy in the required stoichiometric proportions.

In order that the working of processes in accordance with the invention may be fully understood, the preparation of dialkyl alkylphosphonothionates by batch and continuous processes will now be described.

The alkyl phosphonous dichloride used may be methyl phosphonous dichloride or ethylphosphonous dichloride while the alcohol participating in the reaction may be any lower $\text{C}_1\text{—C}_4$ alcohol such as methanol, ethanol, a propanol or a butanol and an alkyl group in the specification means a lower alkyl group containing not more than four carbon atoms. Similarly, the expression alcohol in this specification means an alkanol having not more than four carbon atoms.

The following four examples illustrate a process for producing a dialkyl alkylphosphonothionate which comprises treating the appropriate alkylphosphonous dichloride with elementary sulphur, heating the mixture to a

temperature in the region of its boiling point, slowly adding the appropriate alkanol and maintaining the mixture at this temperature for a further period during which the concentration of dialkyl alkylphosphonothionate over alkyl alkylphosphonochloridothionate progressively increases until a good yield of the dialkyl alkylphosphonothionate is obtained.

EXAMPLE 1

DIETHYL METHYLPHOSPHONOTHIONATE

234 g. (2 mol) of methylphosphonous dichloride are mixed with 64 g. of sulphur flowers in a 500 ml. three necked flask fitted with reflux condenser, stirrer, dropping funnel, thermometer and nitrogen inlet. Nitrogen is passed in a slow stream while the mixture is heated to 75° C. 260 g. (5.65 mol) of ethyl alcohol are then added slowly over a period of the order of half an hour. The mixture may be heated to a temperature maintained between about 75° and 90° C., either under reflux or at a somewhat lower temperature. Copious evolution of hydrogen chloride occurs. After approximately half the alcohol has been added the sulphur almost disappears and the rate of evolution of hydrogen chloride diminishes. Addition of the remainder of the alcohol causes only slight reaction. The almost clear solution is then heated at about 75° C. for two hours. Unchanged alcohol is then removed by distillation under slightly reduced pressure. The residual liquid is fractionated *in vacuo*. 267 g. (an 80% yield) of diethyl methylphosphonothionate are obtained.

EXAMPLE 2

DI-n-PROPYL METHYLPHOSPHONOTHIONATE

234 g. (2 mol) of methylphosphonous dichloride, 64 g. of sulphur and 252 g. (4.2 mol) of n-propyl alcohol are reacted in a manner described in Example 1. The mixture is heated for a total period of 3½ hours. 300 g. (a 77% yield) of di-n-propyl methylphosphonothionate are obtained.

EXAMPLE 3

DI-n-BUTYL METHYLPHOSPHONOTHIONATE

234 g. (2 mol) of methylphosphonous dichloride, 64 g. of sulphur and 444 g. (6.0 mol) of n-butyl alcohol are reacted in a

manner described in Example 1. The mixture is heated for a total period of 3½ hours. 324 g. (a 72% yield) of di-n-butyl methylphosphonothionate are obtained.

5 EXAMPLE 4

DIMETHYL METHYLPHOSPHONOTHIONATE

234 g. (2 mol) of methylphosphonous dichloride, 64 g. of sulphur and 160 g. (5 mol) of methyl alcohol are reacted in a manner described in Example 1. The mixture is heated for a total period of 3 hours. 144 g. (a 51% yield) of dimethyl methylphosphonothionate are obtained. This relatively low yield is probably due to the inherent instability of dimethyl esters in general.

15 A continuous process for the manufacture of a dialkyl alkylphosphonothionate comprises continuously introducing into a reaction vessel containing sulphur an alkyl phosphonous dichloride at a given molar rate and an alkanol at substantially twice the given molar rate, said alkyl groups and alkanol containing not more than four carbon atoms, maintaining the reaction vessel filled with the reaction mixture in the liquid state at a temperature in the region of the boiling point of the reaction mixture whereby hydrogen chloride produced as the reaction proceeds is liberated in the gaseous phase so that its concentration in the liquid reaction phase remains low, and continuously removing from the reaction vessel the reaction product containing dialkyl alkylphosphonothionate.

35 A suitable continuous process for making dialkyl alkylphosphonothionates may be carried out as follows. A tower is packed with rock sulphur cubes of about ½" size and is maintained by a suitable heating jacket at an appropriate temperature in the region of the boiling point of the reaction mixture (80°—90° C. for the production of diethyl methylphosphonothionate) by a suitable heating jacket. The tower is provided with two feed pipes which pass the alkanol and alkylphosphonous dichloride centrally down within the heated tower to the base region whence the reagents are admitted to the reaction mixture already surrounding the sulphur cubes. A constant stream of an inert gas, for example, nitrogen is bubbled through the liquid reaction mixture. Hydrogen chloride is evolved and escapes upwards through the reaction medium and passes out through an outlet vent at the top of the tower.

55 It is important that the supply of alkylphosphonous dichloride and alkanol is maintained as accurately as possible in the stoichiometric proportions of one mol of alkylphosphonous dichloride to two mols of alkanol so that the alkanol is not in excess during the initial stage of the reaction.

The reaction medium containing the crude dialkyl alkylphosphonothionate is allowed to overflow from the top of the tower and pass

65 to a settling tank in which the sulphur settles to leave a clear liquid. The clear liquid may then be degassed and any unreacted alkanol removed by distillation if necessary.

The alkylphosphonous dichloride and alkanol are supplied to the reaction mixture at a steady rate which may be such that the mean residence time of liquid material in the reaction vessel is of the order of twenty minutes, appreciably less than the total reaction time for the batch processes as previously described.

An initial liquid support for the sulphur before the addition of alkanol and alkylphosphonous dichloride may be provided in the form of the dialkyl alkylphosphonothionate which is to be produced by the process and it will be appreciated that such an initial provision is not outside the scope of the invention as the product is soon produced in the reaction mixture.

WHAT WE CLAIM IS:—

1. A process for producing a dialkyl alkylphosphonothionate which comprises forming a mixture of an alkylphosphonous dichloride with elemental sulphur and an alkanol, said alkyl groups and alkanol each containing not more than four carbon atoms, and maintaining the said mixture in the liquid state at a temperature in the region of its boiling point whereby the hydrogen chloride produced as the reaction proceeds is liberated in the gaseous phase so that its concentration in the liquid reaction phase remains low.

2. A process for the manufacture of dialkyl alkylphosphonothionate which comprises forming a mixture of an alkyl phosphonous dichloride with elemental sulphur and an alkanol in such proportions that the alkanol is not in stoichiometric excess, and maintaining the said mixture in the liquid state at a temperature in the region of its boiling point whereby hydrogen chloride produced as the reaction proceeds is liberated in the gaseous phase so that its concentration in the liquid reaction phase remains low, and adding more alkanol until it is present in at least stoichiometric proportions before the completion of the reaction, said alkyl groups and alkanol each containing not more than four carbon atoms.

3. A process for the manufacture of a dialkyl alkylphosphonothionate which comprises forming a mixture of an alkylphosphonous dichloride with elemental sulphur and heating the mixture to a temperature in the region of and below its boiling point, adding an alkanol to the said mixture until it is present in at least stoichiometric proportions to form a resulting mixture which is maintained in the liquid state at a temperature in the region of its boiling point whereby hydrogen chloride produced as the reaction proceeds is liberated in the gaseous phase so that its concentration in the liquid reaction phase remains low, said

alkyl groups and alkanol containing not more than four carbon atoms.

4. A continuous process for the manufacture of a dialkyl alkylphosphonothionate which comprises continuously introducing into a reaction vessel containing sulphur an alkyl phosphonous dichloride at a given molar rate and an alkanol at substantially twice the given molar rate, said alkyl groups and alkanol containing not more than four carbon atoms, maintaining the reaction vessel filled with the reaction mixture in the liquid state at a temperature in the region of the boiling point of the reaction mixture whereby hydrogen chloride produced as the reaction proceeds is liberated in the gaseous phase so that its concentration in the liquid reaction phase remains low, and continuously removing from the reaction vessel the reaction product containing dialkyl alkylphosphonothionate.

5. A process according to any preceding

claim and in which the alkylphosphonous dichloride is either methylphosphonous or ethylphosphonous dichloride.

6. A process according to Claim 4 wherein the alkanol and alkylphosphonous dichloride are introduced into the lower part of the reaction vessel and the reaction mixture is withdrawn through an overflow outlet.

7. A process according to Claim 6 and in which means for bubbling an inert gas through the reaction liquid is provided.

8. A process for making a dialkyl alkylphosphonothionate substantially as hereinbefore described in any one of the Examples 1 to 4.

9. A continuous process for making a dialkyl alkylphosphonothionate substantially as hereinbefore described.

J. V. GOODFELLOW,
Chartered Patent Agent,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Improvements in the manufacture of Dialkyl Alkylphosphonothionates

We, NATIONAL RESEARCH DEVELOPMENT CORPORATION, a British Corporation established by Statute, of 1, Tilney Street, London, W.1, do hereby declare this invention to be described in the following statement:—

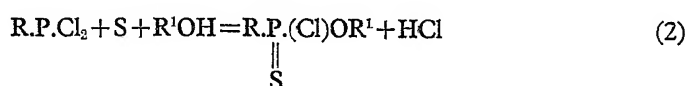
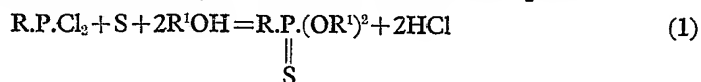
The present invention relates to the manufacture of the dialkyl alkylphosphonothionates, a number of which are used as insecticides.

The invention provides an improved manufacturing process by which the dialkyl alkylphosphonothionates may be synthesised in one step from the appropriate alkylphos-

phonous dichloride, the appropriate alcohol and sulphur.

In accordance with the invention, a process for producing a dialkyl alkylphosphonothionate comprises treating the appropriate alkylphosphonous dichloride with elementary sulphur, heating the mixture to a temperature in the region of its boiling point, slowly adding the appropriate alcohol and maintaining the mixture at this temperature for a further period until a good yield of the dialkyl alkylphosphonothionate is obtained.

It has been established that the following three reactions take place:—

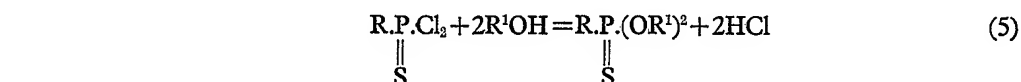
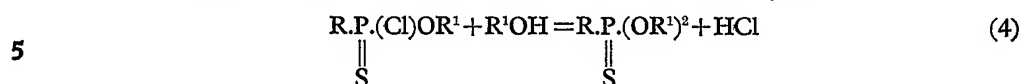


The process is preferably carried out by adding the alcohol slowly over a period of the order of half an hour to a mixture of the alkylphosphonous dichloride in an inert or reducing atmosphere maintained at a temperature close to the boiling point of the mixture so that the hydrogen chloride readily vaporises and its concentration in the liquid reaction phase is low.

In this earlier part of the reaction period all three reactions (1), (2) and (3) proceed, at first the reactions (2) and (3) predominate,

the hydrogen chloride produced catalysing the production of alkylphosphonothionic dichloride in accordance with reaction (3). The maintenance of the mixture at the elevated temperature close to its boiling point for a further period brings about an increase in the concentration of the dialkyl alkylphosphonothionate and a decrease in the concentration of alkyl alkylphosphonochloridothionate produced in accordance with reaction (2) and alkylphosphonothionic dichloride produced in accordance with reac-

tin (3) as these two intermediate products react with alcohol to produce dialkyl alkylphosphonothionate respectively in accordance with the following reactions:—



Generally the order of one hour after the addition of alcohol has been completed is sufficient for the removal of alkylphosphonothionic dichloride. Maintenance of the reaction conditions for a further period progressively increases the concentration of alkyl dialkylphosphonothionate over alkyl alkylphosphonochloridothionate until after about another hour in most cases a concentration of at least 95% of product can be obtained.

The alkylphosphonous dichloride used may be methylphosphonous dichloride or ethylphosphonous dichloride while the alcohol participating in the reaction may be any lower alcohol such as methanol, ethanol, a propanol or a butanol and whenever an alkyl group is referred to in the specification a lower alkyl group is implied.

The process has the advantage that a dialkyl alkylphosphonothionate may be produced in a few hours in one operation without requiring the use of a solvent or any other agent such as a tertiary base for the removal of the liberated hydrogen chloride.

By way of example the preparation of various dialkyl alkylphosphonothionates will now be described.

EXAMPLE 1

DIETHYL METHYLPHOSPHONOTHIONATE
234 g. (2 mole) of methylphosphonous dichloride are mixed with 64 g. of sulphur flowers in a 500 ml. three necked flask fitted with condenser, stirrer, dropping funnel, thermometer and nitrogen inlet. Nitrogen is passed in a slow stream while the mixture is heated to 75° C. 260 g. (5.65 mole) of ethyl alcohol are then slowly added over a period of the order of half an hour, the temperature being maintained between 75° and 85° C. Copious evolution of hydrogen chloride occurs. After approximately half the alcohol has been added the sulphur almost disappears and the rate of evolution of hydrogen chloride

diminishes. Addition of the remainder of the alcohol causes only slight reaction. The almost clear solution is then heated at about 75° C. for two hours. Unchanged alcohol is then removed by distillation under slightly reduced pressure. The residual liquid is fractionated *in vacuo*. 267 g. (an 80% yield) of diethyl methylphosphonothionate are obtained.

EXAMPLE 2

DI-n-PROPYL METHYLPHOSPHONOTHIONATE
234 g. (2 mole) of methylphosphonous dichloride, 64 g. of sulphur and 252 g. (4.2 mole) of n-propyl alcohol are reacted in a manner described in Example 1. The mixture is heated for a total period of 3½ hours. 300 g. (a 77% yield) of di-n-propyl methylphosphonothionate are obtained.

EXAMPLE 3

DI-n-BUTYL METHYLPHOSPHONOTHIONATE
234 g. (2 mole) of methylphosphonous dichloride, 64 g. of sulphur and 444 g. (6.0 mole) of n-butyl alcohol are reacted in a manner described in Example 1. The mixture is heated for a total period of 3½ hours. 324 g. (a 72% yield) of di-n-butyl methylphosphonothionate are obtained.

EXAMPLE 4

DIMETHYL METHYLPHOSPHONOTHIONATE
234 g. (2 mole) of methylphosphonous dichloride, 64 g. of sulphur and 160 g. (5 mole) of methyl alcohol are reacted in a manner described in Example 1. The mixture is heated for a total period of 3 hours. 144 g. (a 51% yield) of dimethyl methylphosphonothionate are obtained. This relatively low yield is probably due to the inherent instability of dimethyl esters in general.

J. V. GOODFELLOW,
Chartered Patent Agent,
Agent for the Applicants.